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Analysis of Polynuclear Aromatic Hydrocarbons in Particulate Matter by Luminescence Techniques

Battelle Columbus Labs., OH

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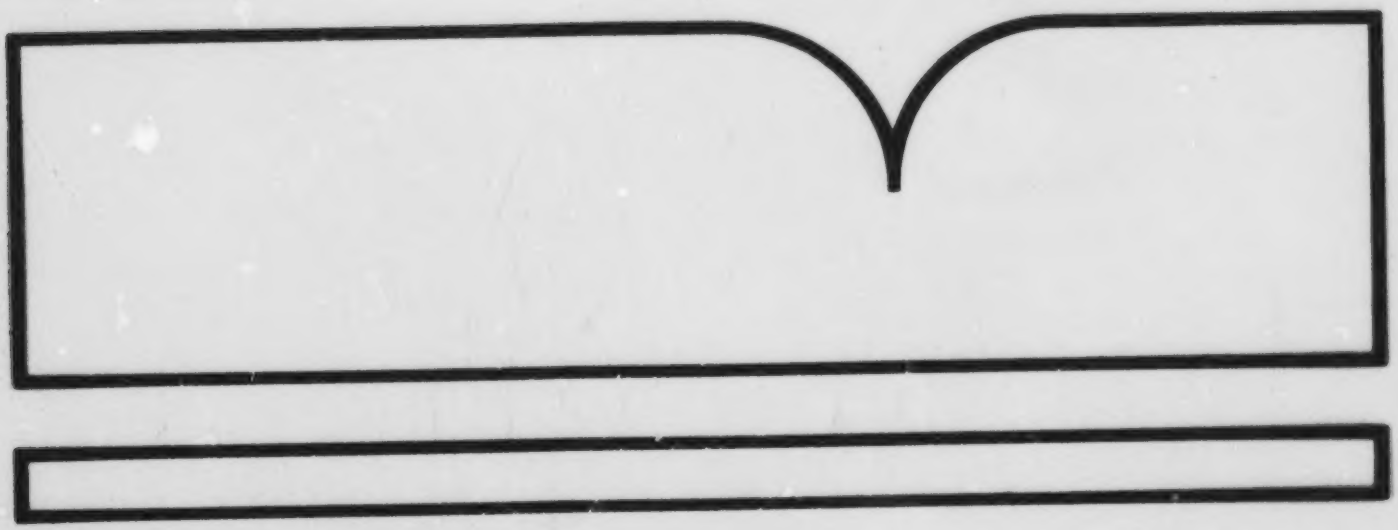

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ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN PARTICULATE MATTER BY LUMINESCENCE TECHNIQUES

by

W. A. Ivancic, L. L. Brown, R. M. Riggin
and R. H. Barnes
Battelle Columbus Laboratories
Columbus, Ohio 43201

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Project Officer

Nancy K. Wilson
Environmental Monitoring Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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16. ABSTRACT

Fluorescence, phosphorescence, and heavy-metal activated room temperature phosphorescence spectra were obtained for ten polycyclic aromatic hydrocarbon (PAH) reference compounds individually and in mixtures on quartz plates and particulate matter. The results indicate that multicomponent analysis of PAHs on airborne particulate matter may be possible with the development of appropriate multicomponent spectral deconvolution procedures. The direct analysis approach in combination with the use of solvent extraction followed by fluorescence analysis can provide a rapid means of analysis for PAHs both within and on the surface of particulate matter. Direct phosphorescence was too weak to be useful at 5-10 μg/g levels found in many types of particulate samples. Heavy-metal activated room-temperature phosphorescence appears more sensitive to matrix and substrate effects and less amenable to multicomponent analysis than fluorescence.

The fluorescence spectrum of benzo(a)pyrene was found to be affected by exposure to low levels of ozone. However, the fluorescence spectrum retains characteristic features that enable identification of the benzo[a] pyrene.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. The direct fluorescence approach investigated in this study has potential for both screening and analyzing polycyclic aromatic hydrocarbons in collected samples of atmospheric particulate materials. The optical approach offers the advantages of being rapid and relatively inexpensive. A rapid means of analyses for polycyclic aromatic compounds on particles will facilitate the monitoring and surveying of pollution sources that contribute to the inventory of polycyclic aromatic hydrocarbons in the environment.

Thomas R. Hauser, Ph.D
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ABSTRACT

An experimental study was conducted to determine if optical fluorescence can be used for the direct analysis of polycyclic aromatic hydrocarbons (PAHs) on particulate materials. Fluorescence measurements were made on 10 reference PAH compounds both individually and in mixtures on quartz surfaces and on particulate materials. The reference compounds investigated were benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, benzo(a)anthracene, chrysene, benzo(ghi)perylene, 1,2,3,4-dibenzanthracene, 1,2,5,6-dibenzanthracene, and fluoranthene. These compounds are typical of the major PAHs found on particulate materials from urban atmospheres. Fluorescence spectra for the different compounds were found to be unique, and individual compounds could be recognized in fluorescence spectra for complex mixtures of the reference compounds. It was concluded that with proper deconvolution and pattern-recognition techniques it should be possible with fluorescence to directly analyze PAH mixtures of the complexity used in this study. Further work is required to determine the potential number of components that can be identified in complex mixtures along with the quantitative accuracy.

Fluorescence analyses were also performed on samples from supercritical CO_2 extracts of particulate materials. The extractions are simple to perform and provide a means both for increasing detection sensitivity and for the analysis of PAHs not only on the surface but also inside particles.

A brief comparison was also made between direct fluorescence and heavy metal activated room temperature phosphorescence for the measurement of PAHs on particulate materials. In general, it was found that fluorescence was more sensitive than the phosphorescence approach and less susceptible to both the type of surface involved and the method of sample preparation.

To assess the possibility of changes in PAHs due to exposure to reactive species in the atmosphere, fluorescence measurements were performed on benzo(a)pyrene on quartz after exposure to 1 ppmvozone for various periods of time up to 42 hours. Ozone exposure appeared to reduce the fluorescence intensity, but the general contours of the spectra and the wavelengths of the major emission peaks remained the same.

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SECTION 1

INTRODUCTION

The purpose of the program described in this report was to evaluate the potential of optical fluorescence and phosphorescence techniques for the direct analysis of polycyclic aromatic hydrocarbons (PAHs) in particulate samples collected from urban atmospheres. Conventional chemical procedures for the analysis of PAHs in particulate matter are time consuming and expensive. If luminescence techniques without involved chemical preparation and extractions can be used successfully for this application, it will greatly enhance the capabilities for the study and survey of carcinogen bearing particulate samples in the environment.

The facts that PAHs tend to be highly luminescent and individually exhibit characteristic spectra suggest that fluorescence and phosphorescence techniques be explored for particulate analysis. These techniques simply involve irradiating a sample with ultraviolet light and analyzing the intensity, spectral profile and timing of the luminescence. Fluorescence emissions generally decay in less than 10 μs after excitation, whereas phosphorescence is characterized by emission lifetimes extending from about 100 μs to minutes. Through selective wavelength excitation coupled with spectral analysis of the luminescence emission, it is often possible to apply multicomponent analysis procedures to identify and quantify individual species in complex mixtures.

As a basis for the studies performed in this program a total of 10 PAH reference compounds were selected from a list reported by Van Vaeck and Von Cauwenberghe[1] as being representative of the major PAHs found on urban atmospheric particulate matter. A list of these compounds and some physical property data for them are presented in Table 1.

TABLE 1. POLYCYCLIC AROMATIC HYDROCARBONS USED AS REFERENCE COMPOUNDS

Polycyclic Aromatic Compounds+	Formula	Structure	M.W.	M.P.°C	B.P.°C	Solid Density g/cm³	Vapor Pressure, Torr 25°C	100°C	300°C	Reference
Benzo(b)fluoranthene (3,4-Benzofluoranthene)	$C_{20}H_{12}$		252.3	168	--	--	--	--	--	
Benzo(k)fluoranthene (11,12-Benzofluoranthene)	$C_{20}H_{12}$		252.3	217	480	--	9.41×10^{-10}	3.64×10^{-5}	81.81	(2)
Benzo(a)pyrene (3,4-Benzopyrene)	$C_{20}H_{12}$		252.3	176.5-177.5	495	--	5.50×10^{-9}	8.14×10^{-5}	49.06	(2)
Benzo(e)pyrene (4,5-Benzopyrene)	$C_{20}H_{12}$		252.3	178-179	--	--	5.56×10^{-9}	8.72×10^{-5}	57.65	(2)
Benzo(a)anthracene (1,2-Benzanthracene)	$C_{18}H_{12}$		228.3	158-59	437.6	1.245	1.10×10^{-7}	1.10×10^{-3}	385.31	(2)
Chrysene (1,2-Benzophenanthrene)	$C_{18}H_{12}$		228.3	255-6	448.0	1.274	4.46×10^{-9}	6.38×10^{-5}	37.15	(1)
Benzo(ghi)perylene (1,12-Benzoperylene)	$C_{22}H_{12}$		276.3	272-273	>500	1.35	1.01×10^{-10}	3.21×10^{-6}	5.659	(2)
1,2,3,4-Dibenzanthracene	$C_{22}H_{14}$		278.4	205	--	--	--	--	--	
1,2,5,6-Dibenzanthracene (Dibenz[a,h]anthracene)	$C_{22}H_{14}$		278.4	262	524	1.28	3.10×10^{-12}	3.14×10^{-7}	2.76	(1)
Fluoranthene (1,2-Benzacenaphthene)	$C_{16}H_{10}$		202.3	109-10	375	1.252	4.94×10^{-6}	2.03×10^{-2}	2094	(3)

(1) Wakayama, N and Inokuchi, H., Bull. Chem. Soc. Jap. 40,2267-2271 (1967)
(2) Murray, J. T., Pottie, R. F., and Pupp. C. Can. J. Chem. 52, 557-563 (1974)
(3) Hoyer, V. H. and Peperle, W. Z. Electrochem, 62, 61-66 (1958)

+ Selected from list of Van Vaeck and Van Cauwenberghe, Atmospheric Environment 12, 2229 (1978).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The conclusions from this study are summarized below:

- Fluorescence spectra for reference PAHs exhibit characteristic peak wavelengths and contours on particulate material that can be used to identify individual PAHs.
- Shifts in fluorescence spectra occur when PAHs are mixed, but the spectra for individual compounds are still recognizable.
- Pattern-recognition and correlation techniques should be useful to resolve multicomponent fluorescence spectra.
- Single PAH compounds can be detected at levels of 2.5 ng on particulate material with the present system. The use of an optimum system should improve sensitivity by at least 10^3. The sensitivity for PAHs in mixtures is yet to be determined.
- Direct room temperature phosphorescence is too weak to be useful for PAH analysis on particulate materials.
- The use of heavy-metal activators increases the sensitivity and selectivity of room temperature phosphorescence. However, the spectra are sensitive to sample preparation procedures. This process is weaker than direct fluorescence with a detection limit of about 160 ng on particles but may be useful in combination with fluorescence. It needs to be investigated further.
- Ozone exposure affects the fluorescence spectrum of benzo(a)pyrene, but characteristic features are still recognizable.
- Solvent extraction is useful for whole particle analysis and for increasing the sensitivity of the analyses.
- Direct fluorescence analysis is useful for measuring PAH mixtures on the surfaces of airborne particulate samples. In combination with super-critical CO_2 extraction and subsequent fluorescence analysis of the extracted residue, it is possible to analyze PAHs both on the surface of and within particulate matter.

An important facet of this study was to determine if particulate matrix effects and energy-transfer processes between different PAHs and other

species would influence multicomponent luminescence spectra to the extent that individual PAH spectra could not be resolved and interpreted. It was established in this study that spectral distortions do occur, but specific patterns and features characteristic of individual PAHs still remain. These characteristic features suggest that the use of luminescence, especially fluorescence, spectroscopy is feasible for the analysis of PAHs on the surface of particulate samples if appropriate pattern-recognition and multicomponent-deconvolution procedures are employed. Room temperature phosphorescence (RTP) spectra with heavy-metal activators were found to be too sensitive to both the substrate and method of doping to be generally useful for such analyses.

It is recommended that the development of laser fluorescence spectroscopy for the direct analysis of PAHs on particulate materials be pursued further. Major emphasis should be on the development of pattern recognition techniques for the multicomponent analysis of complex PAH mixtures.

SECTION 3

FLUORESCENCE/PHOSPHORESCENCE STUDIES

The objectives of this phase of the project were:

- Obtain fluorescence/phosphorescence reference spectra and intensity data at room temperature on quartz substrates for the 10 reference PAHs listed in Table 1.
- Select optimum wavelengths and delay times after excitation for detecting PAHs both as a class and as individual compounds, and develop the pattern recognition and spectral correlation techniques needed for the analysis of complex PAH mixtures.
- Obtain fluorescence/phosphorescence spectra for particulate samples fortified with different levels of both individual PAHs and PAH mixtures.
- Determine the detection limits, precision, accuracy and selectivity of the luminescence techniques as functions of instrumental variables such as laser power and optical collection efficiency.
- Perform fluorescence/phosphorescence measurements on particulate samples analyzed by other techniques and compare the results to those obtained by direct optical techniques.
- Explore the use of simple extraction procedures with luminescence measurements to aid in the analysis of multicomponent PAH mixtures.

Spectroscopic data from Clar[2], Birks[3], Berlman[4] and other literature references were used to determine optimum laser-excitation and luminescence-emission wavelengths for the 10 PAHs listed in Table 1. An energy level diagram is shown in Figure 1 for a typical PAH. This diagram shows a system of singlet (S) electronic levels and a system of triplet (T) electronic levels. Radiative transitions between singlet and triplet states occur with a much lower probability than transitions between singlet-singlet and triplet-triplet states. Each electronic level has superimposed on it a manifold of vibrational levels with smaller separations. At room temperature, the lower vibrational levels in the ground-state singlet state (S_0) are normally the only levels populated. To detect PAHs by luminescence, an excitation source such as the laser used for this study causes electronic transitions from the S_0 state to a vibrational level in an excited singlet state (S_n).

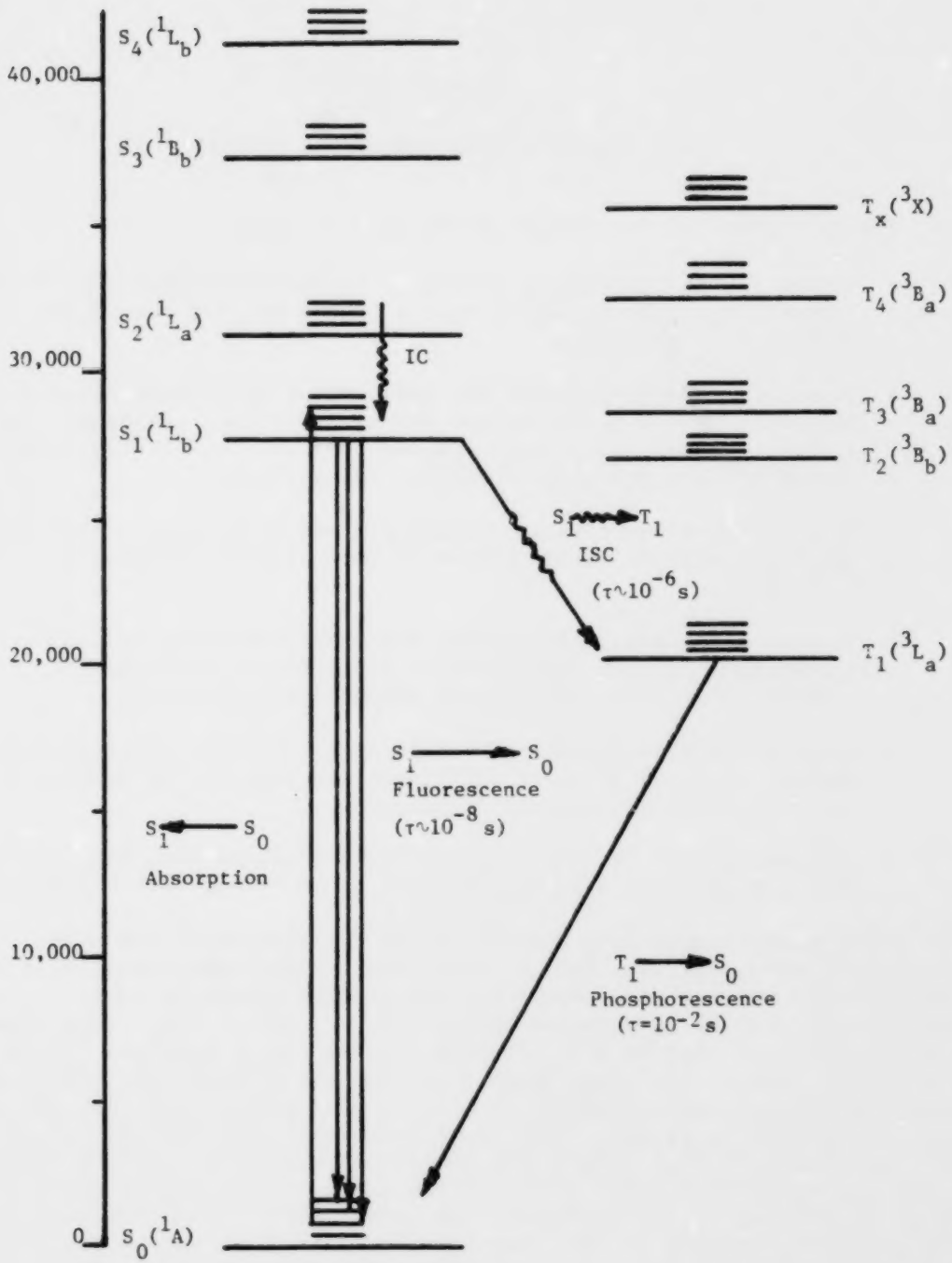


Figure 1. Energy-level diagram for chrysene.

Normally, in polyatomic molecules such as the PAHs, the excited molecules lose energy by nonradiative internal conversion (IC) processes and drop rapidly to the lowest vibrational level in the excited singlet state, where transitions can then occur either to a lower singlet level such as S_0 with accompanying fluorescence emissions, or to a triplet state by intersystem crossing (ISC), a nonradiative process. Molecules in the triplet system cascade rapidly to the lowest vibrational level of the excited triplet state (T_1) from which transitions occur back to the S_0 state, with accompanying phosphorescence emission. Phosphorescence is generally a much slower process than fluorescence. Typical rate constants for fluorescence and phosphorescence are 10^6-10^9 and 10^{-2}-$10^4 s^{-1}$, respectively. Rate constants for IC, S → T ISC, and T → S ISC transitions are 10^{13}-10^{12}, 10^4-10^{12}, and 10^{-4}-$10^5 s^{-1}$, respectively. Vibrational relaxation within an electronic state has a typical rate constant of $>10^{12} s^{-1}$. In cases where the singlet-triplet energy gap is small T → S transition rates can be sufficiently large to generate delayed fluorescence from excited S states.

Phosphorescence intensities in certain cases can be increased by heavy-metal activation. The presence of heavy metals enhances spin-orbit coupling in PAH molecules and thus increases the rate of singlet-to-triplet transitions. Heavy-atom activated phosphorescence, however, is more sensitive than fluorescence to matrix effects.

EXPERIMENTAL PROCEDURES

The laser system used for the luminescence measurements is shown schematically in Figure 2. The laser consists of a Molectron® Model DL 14 dye laser pumped by a Model UV-24 pulsed nitrogen laser (Molectron Corporation, Sunnyvale, CA). The dye laser covers the wavelength range from 360 to beyond 900 nm. With frequency doubling, this range is extended down to 217 nm. The pumping efficiency of the dye laser is about 15 percent with a temporal half width of 6-8 ns for the output pulse and a spectral band-width of 0.01 nm. The doubling efficiency runs from one to several percent depending on the type of nonlinear crystal used. At 292 nm, the excitation wavelength for most of the luminescence measurements in this study, the pulse energy was 2 to 5 μJ.

The samples used for these studies were deposits formed by evaporating PAH solutions on S1-UV low-fluorescence quartz plates (ESCO Products, Inc., Oak Ridge, NJ) or on particles which were sandwiched between two quartz plates. The quartz plates were positioned horizontally, with the laser beam directed down onto the sample at an angle of 70° from the normal to the surface of the quartz plate. Luminescence was collected in the normal direction with f/4 optics and transmitted to a f/9 1.26-M SPEX® Model 1269 spectrometer (SPEX Industries Inc., Metuchen, NJ). The magnification of the optics from the sample to the spectrometer entrance slits was 1 to 2.2. The entrance slits of the spectrometer were aligned in the same plane as the laser beam to permit maximum collection of luminescence from an elongated laser-beam image on the sample surface. The spectrometer was equipped with a 1200 groove/nm grating blazed at 300 nm. The detector used with the spectrometer was a RCA® C31034A photomultiplier (RCA, Lancaster, PA) in a thermoelectrically cooled housing. A 1:1 magnification transfer lens was

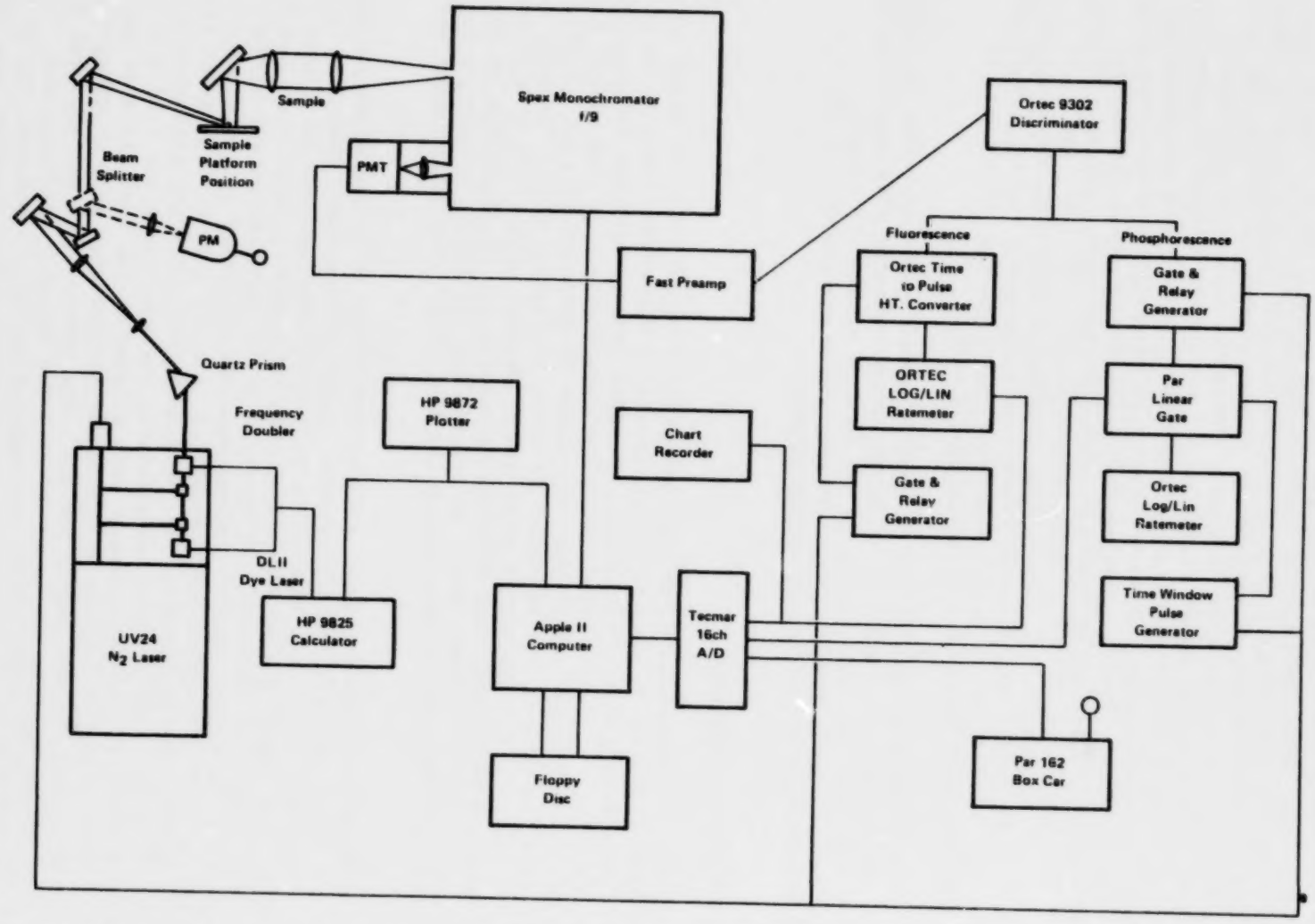


Figure 2. Schematic diagram of laser system for fluorescence and phosphorescence measurements.

used between the exit slits and the photomultiplier. The signal from the photomultiplier was processed by ORTEC 9300 photon counting modules (ORTEC Incorporated, Oak Ridge, TN) with the output fed through an analog-to-digital converter to an Apple® II computer for storage, data processing, and plotting. Details of the signal processing electronics are shown in Figure 2. A dual photon counting system was used so that fluorescence and phosphorescence spectra could be recorded together. The Apple II computer also controlled wavelength scanning of both the dye laser and spectrometer. This arrangement allowed luminescence emission, luminescence excitation and synchronous spectra along with multiple channel data collection to be recorded automatically. Data processing routines included spectral normalization, smoothing and subtraction and multiple-scan signal averaging.

The photon counting system was synchronized to the laser pulse. The detection windows were gated with separate delays so that the system could detect photons at any time after the laser pulse with a variable time window. The output from the dye laser was monitored and used to normalize the luminescence spectra to correct for variations in the dye laser output.

RESULTS

This section presents the results of the luminescence measurements for PAHs on quartz surfaces and particulate materials. In general, fluorescence with very little direct phosphorescence was observed.

Spectra for PAHs on Quartz Plates

To prepare the deposited samples for the luminescence measurements, known weights of PAHs were dissolved in acetone to give concentrations of 100 ppm. Each solution was slowly deposited on an S1-UV quartz plate with a motor-driven hypodermic syringe and allowed to evaporate to dryness. This procedure was designed to produce small uniform deposits of reproducible size. With deposition rates of about 1 µL/min., a ring with an outer diameter of 2 mm was formed. The deposits weighed 0.4-0.6 µg. After drying, the deposits were covered by a second quartz plate to prevent loss of material during handling. Deposits of PAH mixtures were prepared from mixtures of PAHs in a single solution.

For luminescence measurements, the beam from the dye laser was focused on the sample to an area of 0.3 mm x 1 mm so as to illuminate about 20 percent of the area of the deposited ring. The effective amount of PAH detected in these experiments was about 80 ng.

Fluorescence spectra excited at 292 nm for the 10 reference PAH compounds are presented in Figures 3 through 12. The timing window on the detector was set to open 10 ns before the laser pulse and remain open for 60 ns. Most of the fluorescence occurs nearly simultaneously with the laser pulse. Each spectrum exhibited characteristic features that identified the individual compounds. The spectra were recorded by stepping the spectrometer wavelength in 1-nm increments with counting times of 4 s for each increment. A total of 35 min was required to scan 200 nm. In the cases of

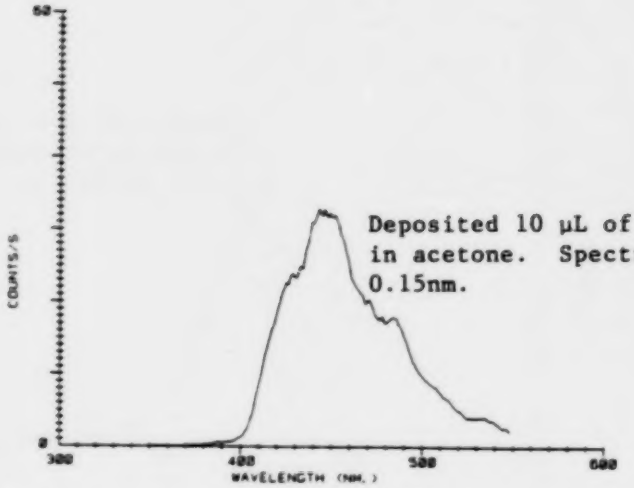


Figure 3. Fluorescence reference spectrum excited at 292 nm for benzo(b)fluoranthene on quartz.

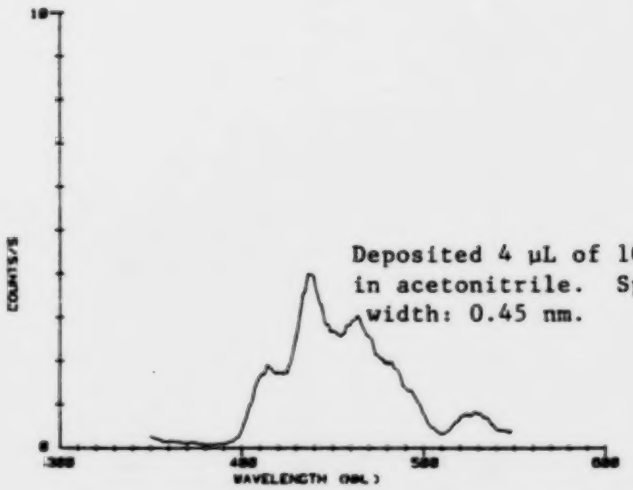


Figure 4. Fluorescence reference spectrum excited at 292 nm for benzo(k)fluoranthene on quartz.

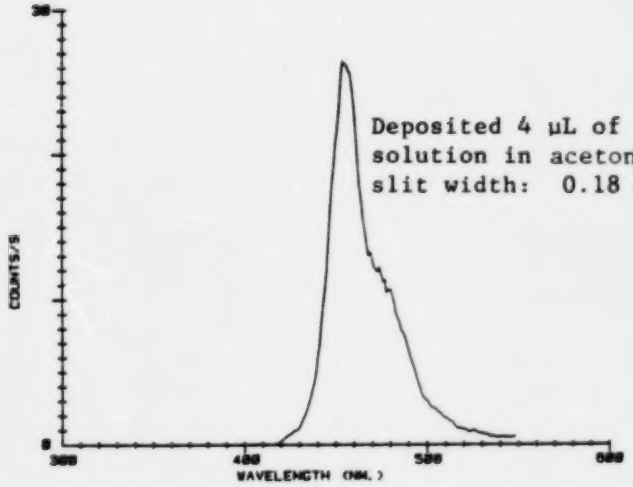


Figure 5. Fluorescence reference spectrum excited at 292 nm for benzo(a) pyrene on quartz.

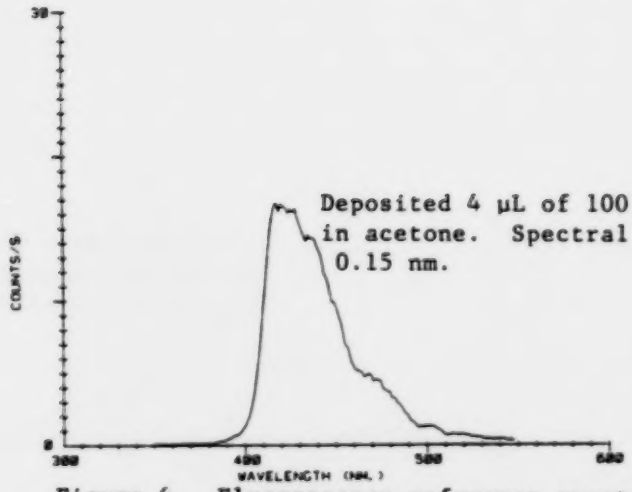


Figure 6. Fluorescence reference spectrum excited at 292 nm for benzo(e) pyrene on quartz.

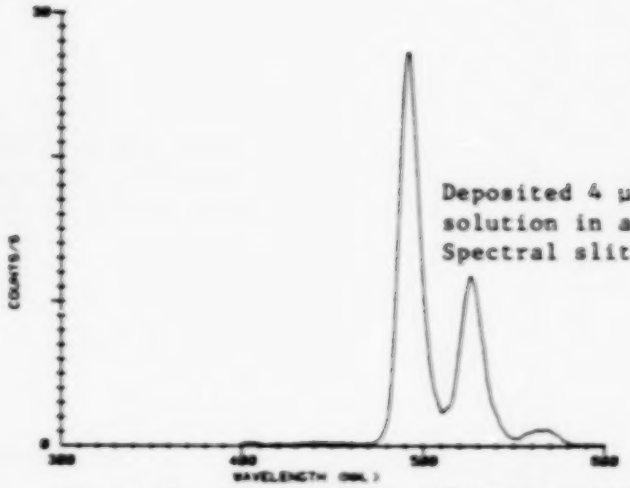


Figure 7. Fluorescence reference spectrum excited at 292 nm for benz(a) anthracene on quartz.

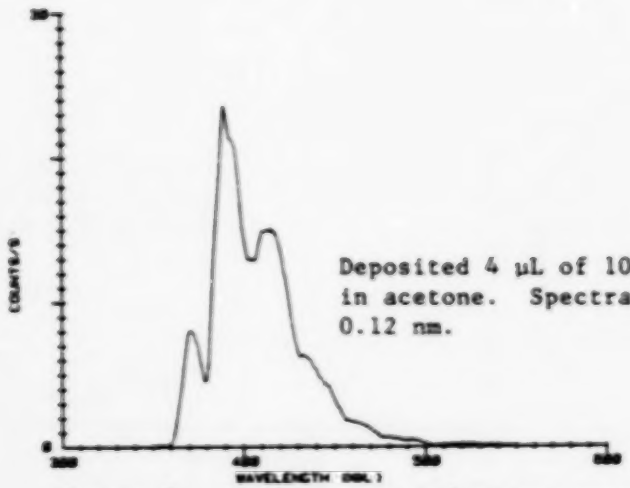
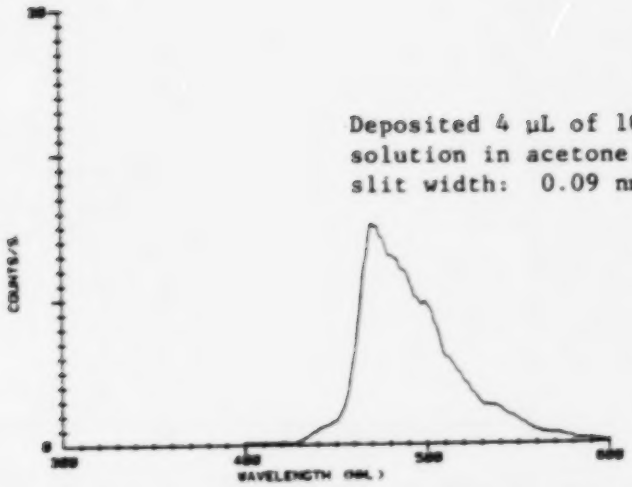
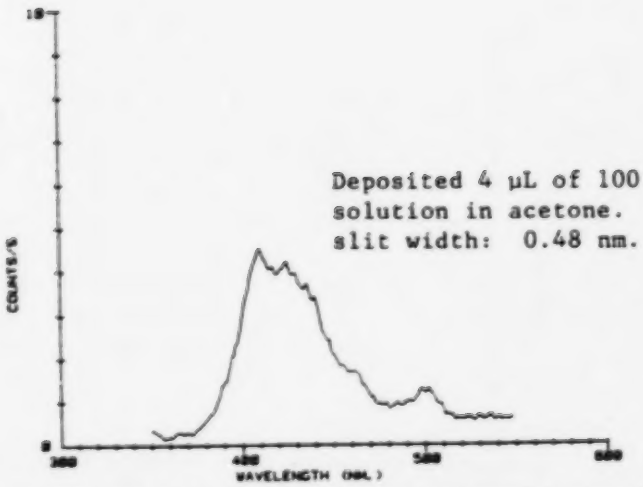


Figure 8. Fluorescence reference spectrum excited at 292 nm for chrysene on quartz.



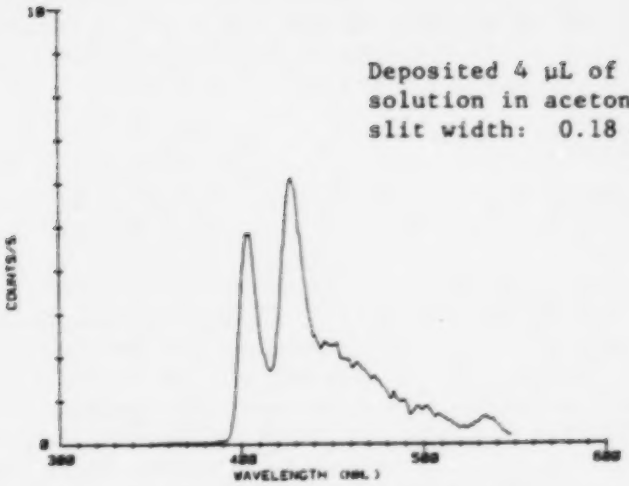
Deposited 4 µL of 100 ppm solution in acetone. Spectral slit width: 0.09 nm.

Figure 9. Fluorescence reference spectrum excited at 292 nm for benzo(ghi) perylene on quartz.



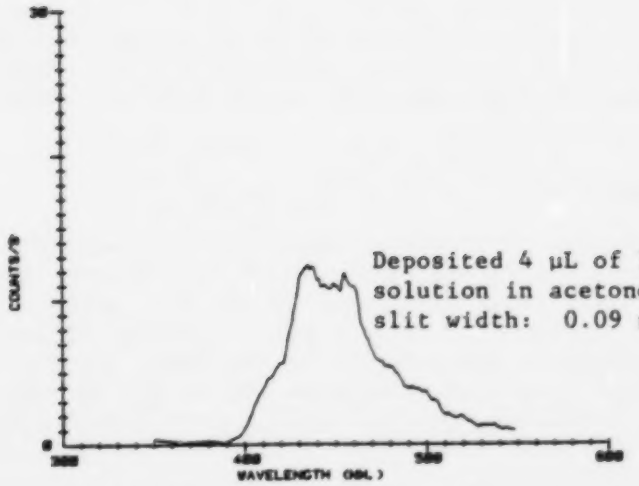
Deposited 4 µL of 100 ppm solution in acetone. Spectral slit width: 0.48 nm.

Figure 10. Fluorescence reference spectrum excited at 292 nm for 1,2,3,4-dibenzanthracene on quartz.



Deposited 4 µL of 100 ppm solution in acetone. Spectral slit width: 0.18 nm.

Figure 11. Fluorescence reference spectrum excited at 292 nm for 1,2,5,6-dibenzanthracene on quartz.



Deposited 4 µL of 100 ppm solution in acetone. Spectral slit width: 0.09 nm.

Figure 12. Fluorescence reference spectrum excited at 292 nm for fluoranthene on quartz.

benzo(a)pyrene, chrysene, and, to a lesser extent, some of the other compounds, spectral intensities of the peaks and contours of the vibronic bands were somewhat sensitive to variations in sample preparation and aging. However, the spectra still retained peaks characteristic of the individual compounds that can be used for their identification.

The fluorescence spectra for PAH mixtures on quartz plates are given in Figures 13 to 16. It is readily observed that mixing compounds results in spectral changes, but it is possible to distinguish the contributions of the individual PAHs to the mixture spectra.

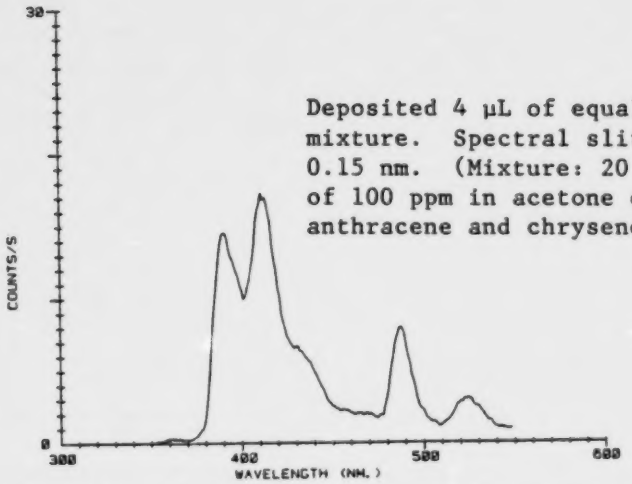
PAH Spectra on Fly Ash

Reference spectra for individual PAHs spiked on NBS standard SRM-1633 fly ash material are shown in Figures 17 to 26. The PAH mixture spectra are given in Figures 27 to 32. The fly ash was fortified by placing weighed amounts of the particulate material on aluminum foil and repeatedly doping the fly ash with 0.5 μL volumes of the 100 ppm PAH solution. Between additions, the doped material was allowed to air dry for 30 s. After the final addition of dopant, the fly ash was air dried for 5 minutes and sandwiched between two S1-UV quartz plates. Two weights of fly ash were used for samples: approximately 5 mg and 15 mg. The 5 mg sample covered an area with a diameter of 5 mm. With the 0.3 mm diameter laser beam, it was possible to measure fluorescence from different locations on the samples. Some loss of PAH to the aluminum foil did occur during spiking, and the PAH was not always distributed evenly over the fly ash.

Fluorescence spectra for PAHs on fly ash showed differences from the spectra of the quartz-deposited material, but recognizable correspondences predominated. The spectral differences are mainly due to matrix/surface effects similar to solvent effects in solution. The amount of PAH detected in the spiked fly ash experiments was about 50 ng. Actual detection limits are nearly two orders-of-magnitude below this level. The high levels of PAHs were used to produce high-intensity spectra with well-defined spectral shapes.

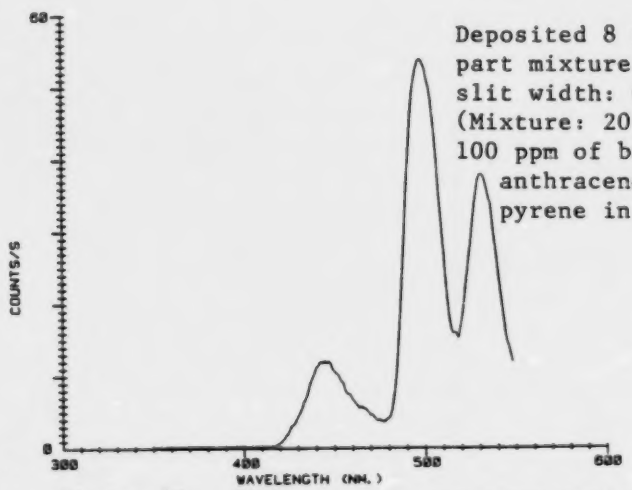
Fly Ash Analyses

National Bureau of Standards (NBS) SRM-1633 and SRM-1648 particulate reference materials were analyzed using direct fluorescence. The spectra for the two samples are shown in Figures 33 and 34. Spectra for SRM-1633 showed no evidence of detectable levels of PAHs; however, fluorescence was observed at shorter wavelengths than emitted by the PAHs. As a class, the PAHs generally produce fluorescence between 380 to 650 nm when excited at 292 nm. The fluorescence from the SRM-1633 peaked at 350 nm, indicating the presence of materials other than PAHs. The results for SRM-1648 showed fluorescence in the PAH region; however, the spectra were not intense enough to permit identification of specific compounds. Prior analyses by extraction and gas chromatography/mass spectrometry gave the analysis in Table 2.



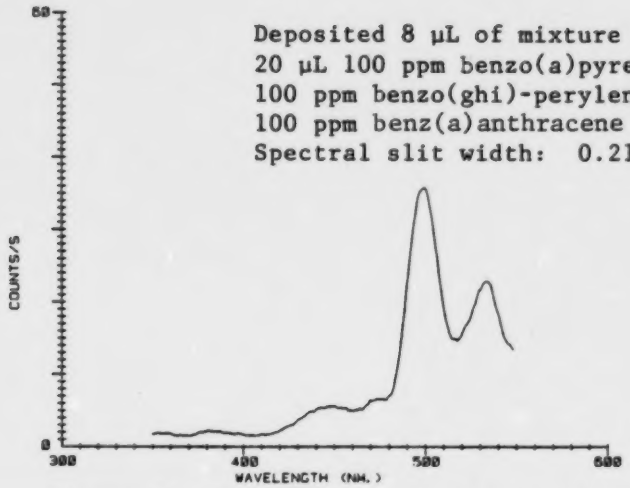
Deposited 4 µL of equal part mixture. Spectral slit width: 0.15 nm. (Mixture: 20 µL each of 100 ppm in acetone of benz(a)-anthracene and chrysene).

Figure 13. Fluorescence spectrum excited at 292 nm for equal part mixture of chrysene and benz(a)anthracene on quartz.



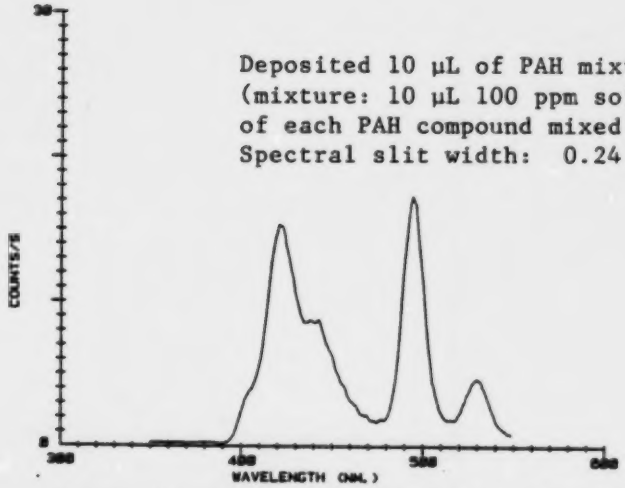
Deposited 8 µL of equal part mixture. Spectral slit width: 0.15 nm. (Mixture: 20 µL each of 100 ppm of benzo(a) anthracene and benz(a) pyrene in acetone).

Figure 14. Fluorescence spectrum excited at 292 nm for equal part mixture of benzo(a) pyrene and benz(a)anthracene on quartz.



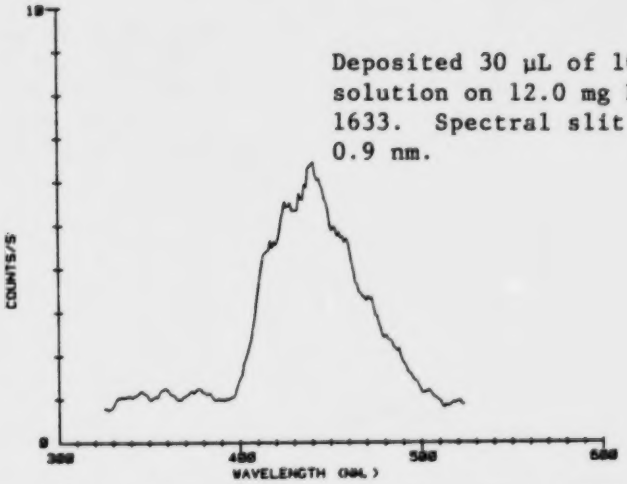
Deposited 8 µL of mixture (mixture: 20 µL 100 ppm benzo(a)pyrene, 20 µL 100 ppm benzo(ghi)-perylene and 20 µL 100 ppm benz(a)anthracene in acetone). Spectral slit width: 0.21 nm.

Figure 15. Fluorescence spectrum excited at 292 nm for equal part mixture of benzo(a)pyrene, benzo(ghi)-perylene and benz(a)anthracene on quartz.



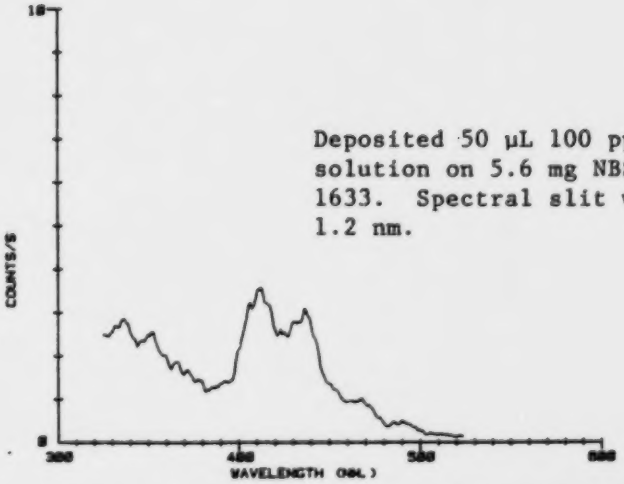
Deposited 10 µL of PAH mixture (mixture: 10 µL 100 ppm solution of each PAH compound mixed together). Spectral slit width: 0.24 nm.

Figure 16. Fluorescence spectrum excited at 292 nm for equal part mixture of all 10 PAH reference compounds on quartz.



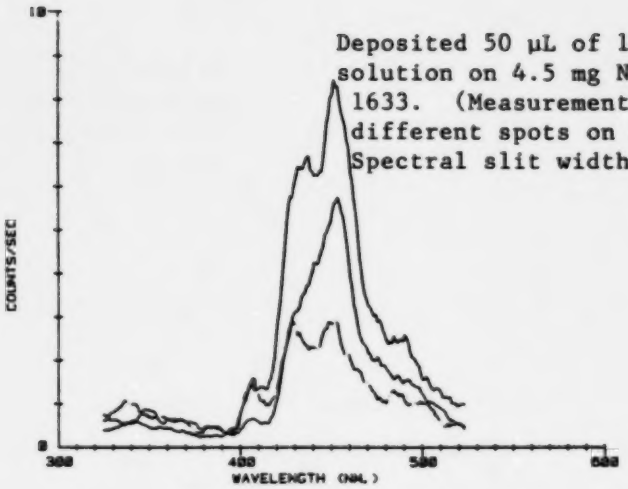
Deposited 30 µL of 100 ppm solution on 12.0 mg NBS SRM 1633. Spectral slit width: 0.9 nm.

Figure 17. Fluorescence spectrum excited at 292 nm for benzo(b) fluoranthene on NBS SRM 1633.



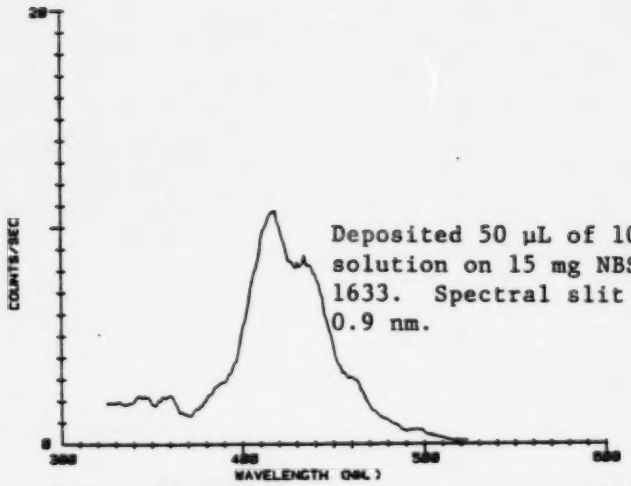
Deposited 50 µL 100 ppm solution on 5.6 mg NBS SRM 1633. Spectral slit width: 1.2 nm.

Figure 18. Fluorescence spectrum excited at 295 nm for benzo(k)fluoranthene on NBS SRM 1633.



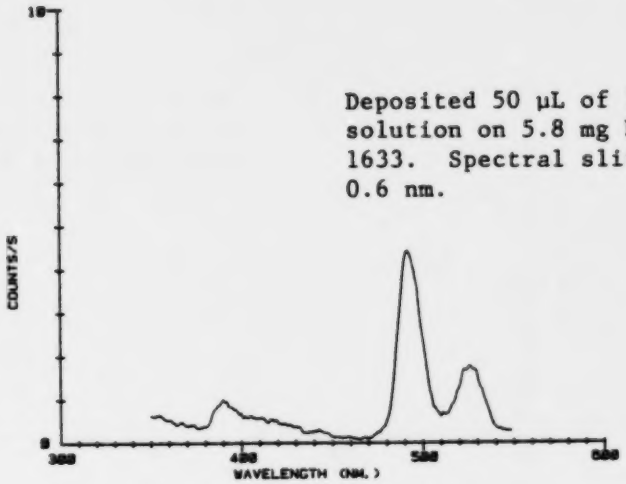
Deposited 50 µL of 100 ppm solution on 4.5 mg NBS SRM 1633. (Measurements at three different spots on slide) Spectral slit width: 0.9 nm.

Figure 19. Fluorescence spectrum excited at 295 nm for benzo(a)pyrene on NBS SRM 1633.



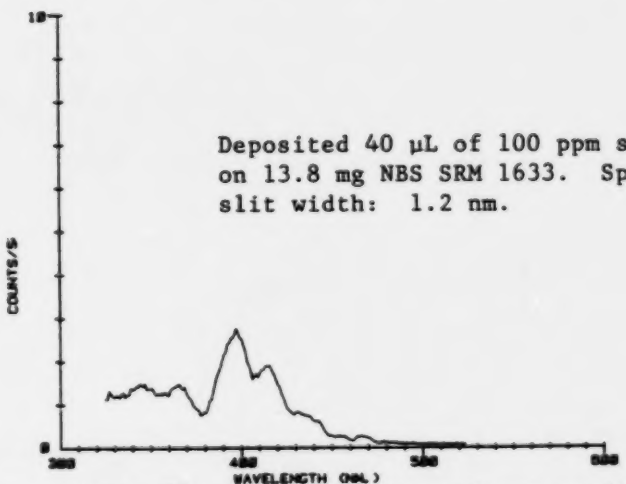
Deposited 50 µL of 100 ppm solution on 15 mg NBS SRM 1633. Spectral slit width: 0.9 nm.

Figure 20. Fluorescence spectrum excited at 295 nm for benzo(e)pyrene on NBS SPM 1633.



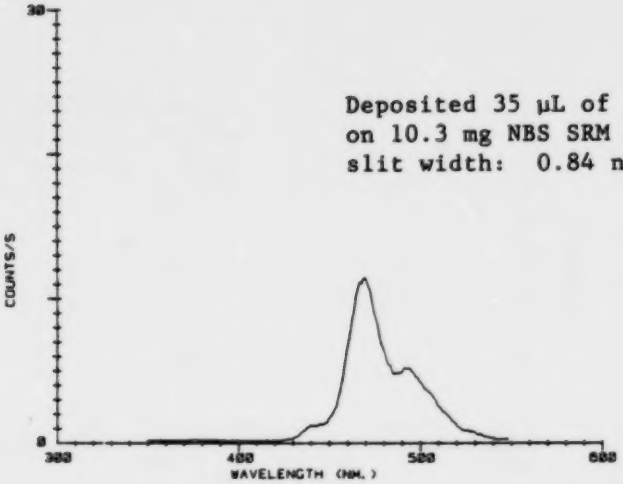
Deposited 50 µL of 100 ppm solution on 5.8 mg NBS SRM 1633. Spectral slit width: 0.6 nm.

Figure 21. Fluorescence spectrum excited at 295 nm for benz(a)anthracene on NBS SRM 1633.



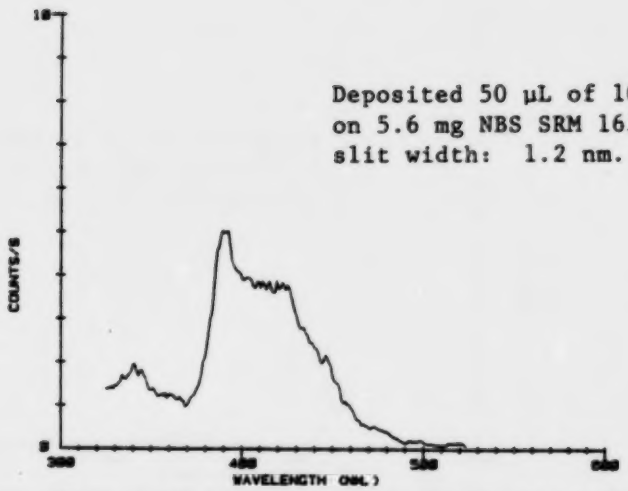
Deposited 40 µL of 100 ppm solution on 13.8 mg NBS SRM 1633. Spectral slit width: 1.2 nm.

Figure 22. Fluorescence spectrum excited at 295 nm for chrysene on NBS SRM 1633.



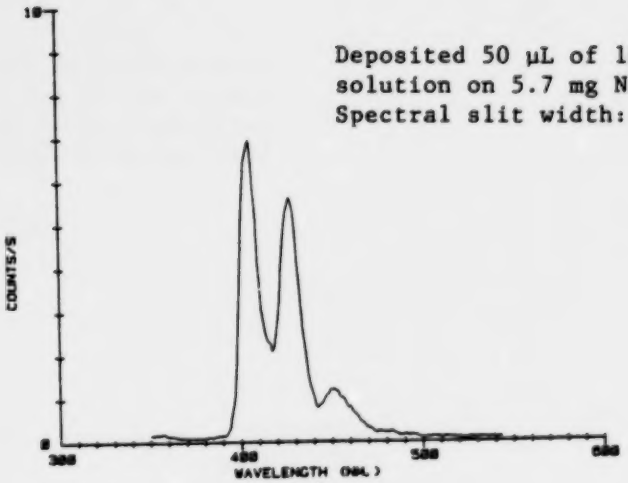
Deposited 35 µL of 100 ppm solution on 10.3 mg NBS SRM 1633. Spectral slit width: 0.84 nm.

Figure 23. Fluorescence spectrum excited at 295 nm for benzo(ghi)perylene on NBS SRM 1633.



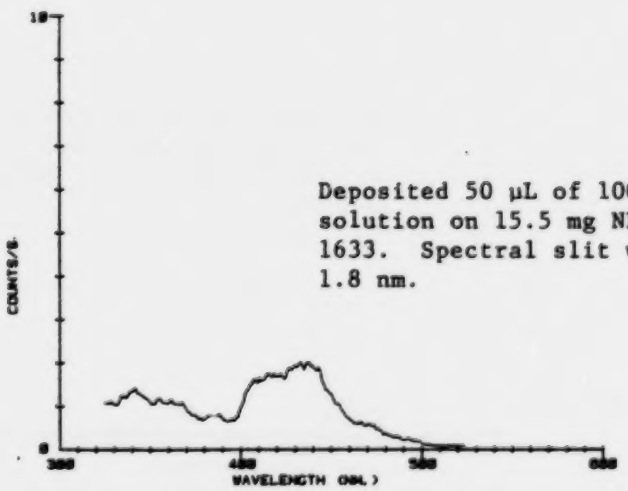
Deposited 50 µL of 100 ppm solution on 5.6 mg NBS SRM 1633. Spectral slit width: 1.2 nm.

Figure 24. Fluorescence spectrum excited at 295 nm for 1,2,3,4-dibenzanthracene on NBS SRM 1633.



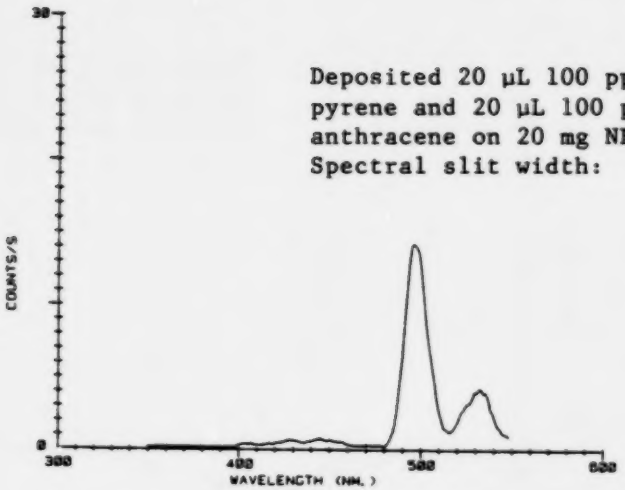
Deposited 50 µL of 100 ppm solution on 5.7 mg NBS SRM 1633. Spectral slit width: 0.3 nm.

Figure 25. Fluorescence spectrum excited at 295 nm for 1,2,5,6-dibenzanthracene on NBS SRM 1633.



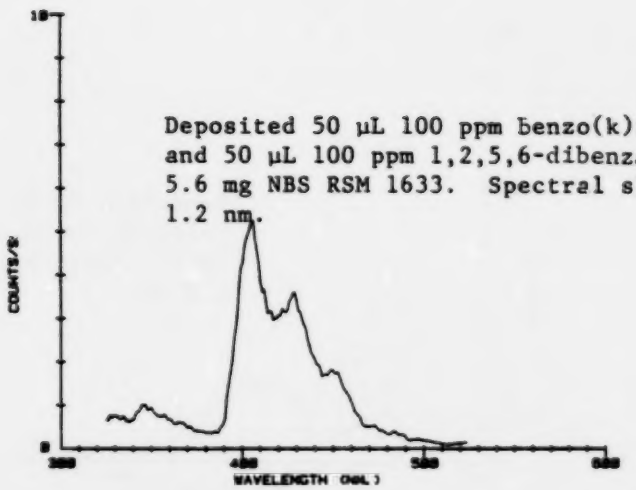
Deposited 50 µL of 100 ppm solution on 15.5 mg NBS SRM 1633. Spectral slit width: 1.8 nm.

Figure 26. Fluorescence spectrum excited at 295 nm for fluoranthene on NBS SRM 1633.



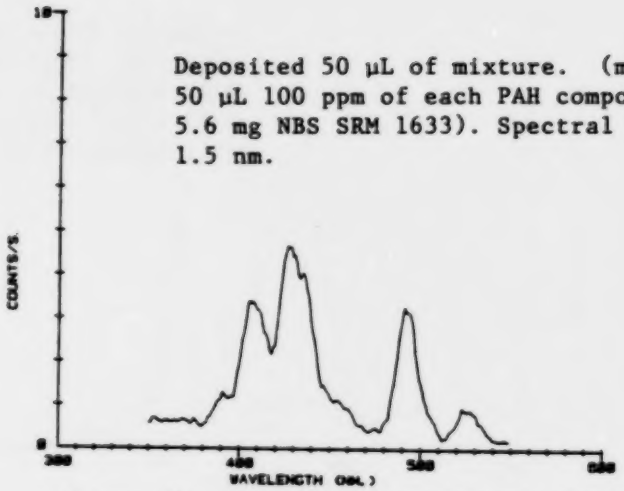
Deposited 20 µL 100 ppm benzo(a) pyrene and 20 µL 100 ppm benz(a) anthracene on 20 mg NBS SRM 1633. Spectral slit width: 0.72 nm.

Figure 27. Fluorescence spectrum excited at 292 nm for equal part mixture of benzo(a)pyrene and benz(a) anthracene on NBS SRM 1633.



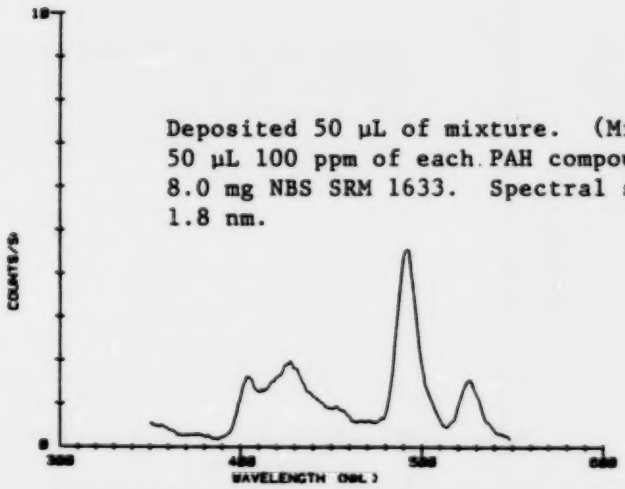
Deposited 50 µL 100 ppm benzo(k)fluoranthene and 50 µL 100 ppm 1,2,5,6-dibenzanthracene on 5.6 mg NBS RSM 1633. Spectral slit width: 1.2 nm.

Figure 28. Fluorescence spectrum excited at 292 nm for equal part mixture of benzo(k) fluoranthene and 1,2,5,6-dibenzanthracene on NBS SRM 1633.



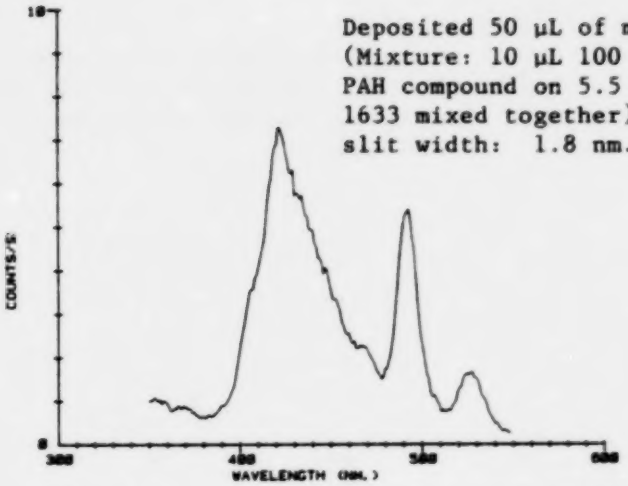
Deposited 50 µL of mixture. (mixture: 50 µL 100 ppm of each PAH compound on 5.6 mg NBS SRM 1633). Spectral slit width: 1.5 nm.

Figure 29. Fluorescence spectrum excited at 292 nm for equal part mixture of benzo(k)fluoranthene, benz(a) anthracene and 1,2,5,6-dibenz-anthracene on NBS SRM 1633.



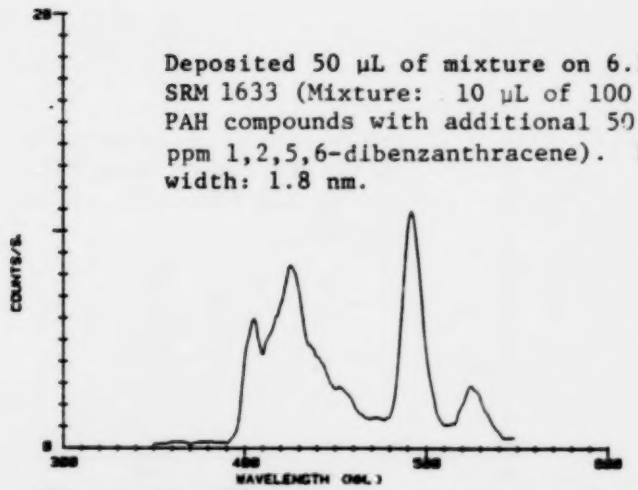
Deposited 50 µL of mixture. (Mixture: 50 µL 100 ppm of each PAH compound on 8.0 mg NBS SRM 1633. Spectral slit width: 1.8 nm.

Figure 30. Fluorescence spectrum excited at 292 nm for equal part mixture of benzo(k)fluoranthene, benzo(a)-pyrene, benz(a)anthracene and 1,2,5,6-dibenzanthracene on NBS SRM 1633.



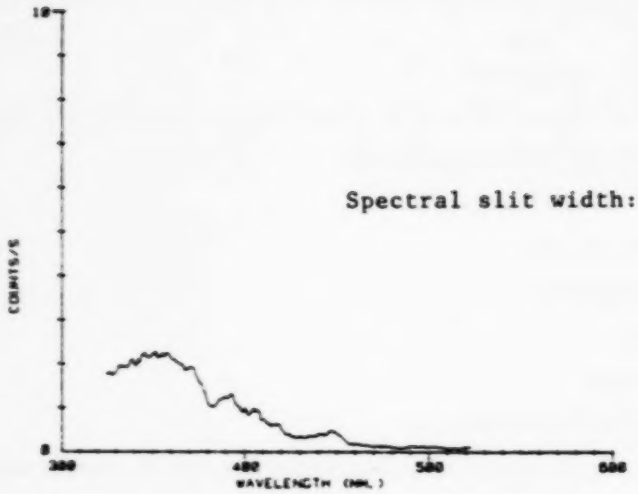
Deposited 50 µL of mixture. (Mixture: 10 µL 100 ppm of each PAH compound on 5.5 mg NBS SRM 1633 mixed together). Spectral slit width: 1.8 nm.

Figure 31. Fluorescence spectrum excited at 292 nm for equal part mixture of 10 PAH reference compounds on NBS SRM 1633.



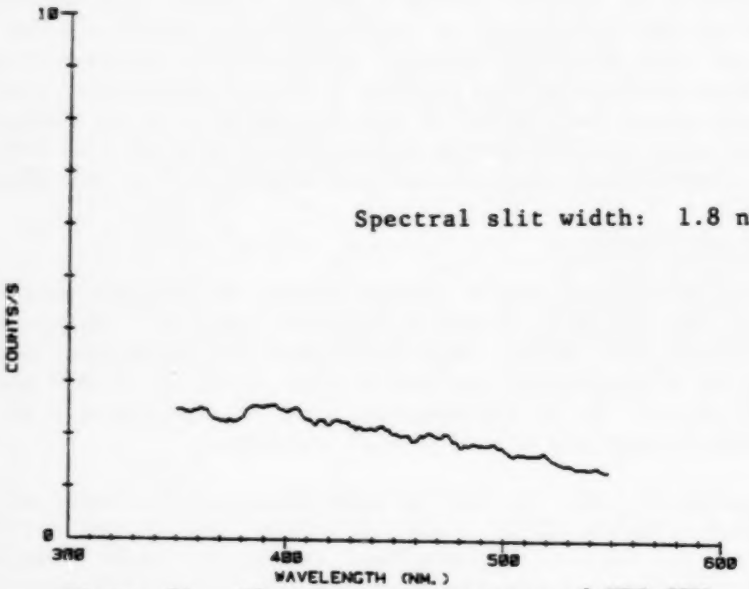
Deposited 50 µL of mixture on 6.1 mg of NBS SRM 1633 (Mixture: 10 µL of 100 ppm each of PAH compounds with additional 50 µL of 100 ppm 1,2,5,6-dibenzanthracene). Spectral slit width: 1.8 nm.

Figure 32. Fluorescence spectrum excited at 292 nm for equal part mixture of 10 PAH reference compounds plus additional 1,2,5,6-dibenzanthracene on NBS SRM 1633.



Spectral slit width: 1.8 nm.

Figure 33. Fluorescence spectrum of NBS SRM 1633 excited at 292 nm.



Spectral slit width: 1.8 nm.

Figure 34. Fluorescence spectrum of NBS SRM 1648 excited at 292 nm.

TABLE 2. PAH CONCENTRATIONS IN NBS PARTICULATE STANDARD SRM-1648 BY EXTRACTION GC-MS

PAH Compound	Concentration µg/g
Benzo(b,k,j)fluoranthenes	13.5
Benzo(a,e)pyrenes	7.4
Fluoranthene	5.7
Phenanthrene	4.8
Pyrene	4.8
Chrysene	4.7
Benzo(a)anthracene	2.5

Soxhlet Extraction Procedure

A high-pressure Soxhlet extractor (J & W Scientific, Orangevale, CA) was used to extract NBS SRM-1633. Approximately 0.5 g of the sample was placed in an extraction thimble in the Soxhlet assembly and supercritical liquid CO_2 was used as the extractant to ensure full extraction. The process was allowed to take place for 2 days. Fluorescence spectra for the extracted particulate sample and the residue from the extraction solvent deposited on quartz are shown in Figures 35 and 36, respectively. The extracted particles exhibited only low background fluorescence whereas the solvent residue showed intense fluorescence similar to that observed from the unextracted material.

Analysis of Results

Only relatively simple deconvolution techniques were explored in this study for the analysis of multicomponent spectra. More sophisticated methods are available,[24] which, when developed appropriately, should make it possible to successfully perform direct analysis of PAH mixtures on particulate materials. It is recommended that the development of these techniques be pursued beyond the scope of this program.

Figures 37, 38, 39, and 40 show examples of simple weighted subtraction procedures. Figure 37 is a simple subtraction of the fly-ash fluorescence background for benzo(k)fluoranthene on NBS SRM 1633. Comparison of the subtracted spectrum with the spectrum for benzo(k)fluoranthene on quartz in Figure 4 shows the effects of the matrix or surface on the spectrum. Similarities between the subtraction result and the spectrum of the compound in the matrix by itself are seen by comparing Figure 37 with Figure 18. In Figure 38, the spectrum for benzo(k)fluoranthene is subtracted from a binary mixture of this compound with 1,2,5,6-dibenzanthracene. The subtracted

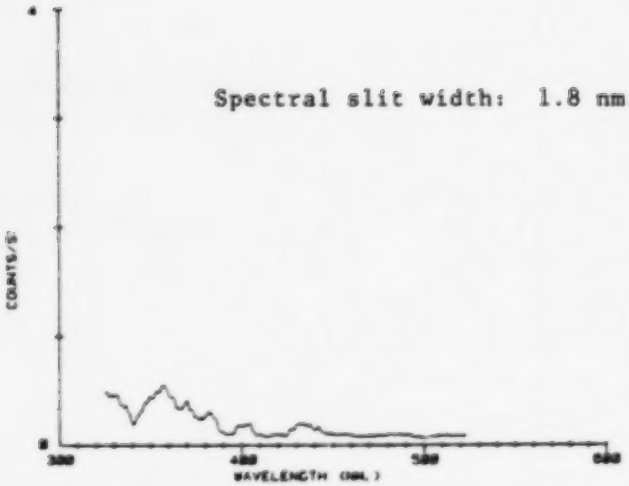


Figure 35. Fluorescence spectrum excited at 292 nm for NBS SRM 1633 after extraction with high-pressure Soxhlet extractor.

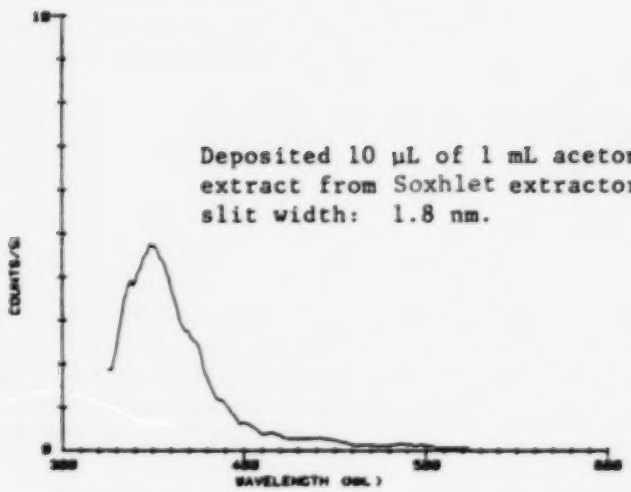
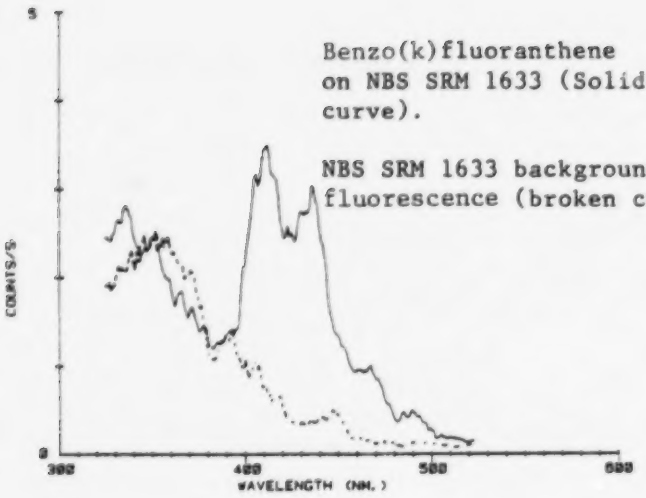


Figure 36. Fluorescence spectrum of extract from NBS SRM 1633.



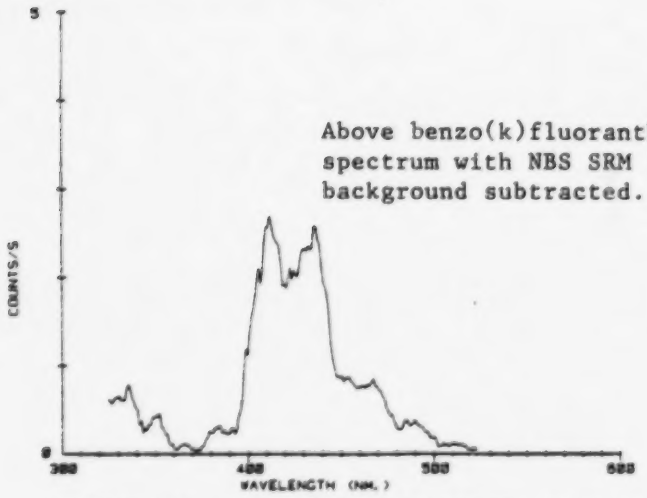
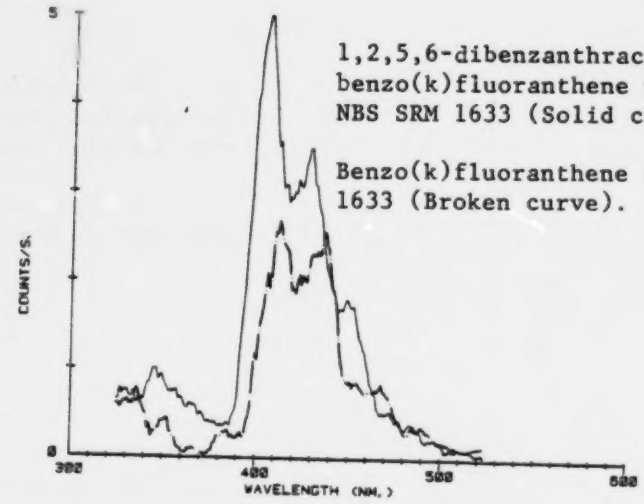
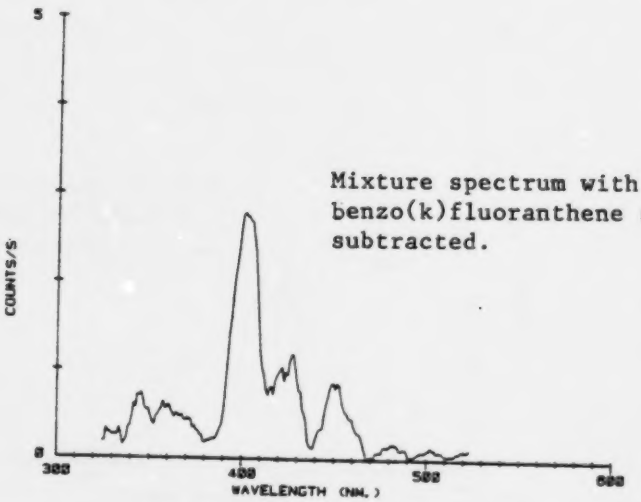


Figure 37. Benzo(k)fluoranthene fluorescence spectrum excited at 292 nm corrected by subtraction of NBS SRM 1633 background.



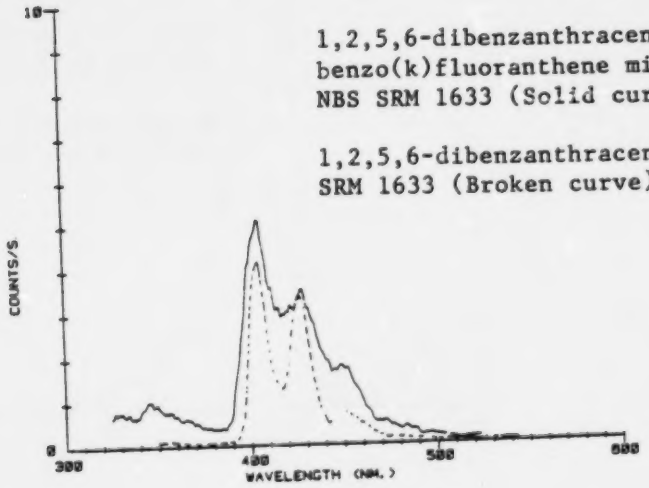
1,2,5,6-dibenzanthracene and benzo(k)fluoranthene mixture on NBS SRM 1633 (Solid curve).

Benzo(k)fluoranthene on NBS SRM 1633 (Broken curve).



Mixture spectrum with above benzo(k)fluoranthene spectrum subtracted.

Figure 38. Subtraction of fluorescence components excited at 292 nm of equal parts benzo(k)-fluoranthene and 1,2,5,6-dibenzanthracene on NBS SRM 1633.



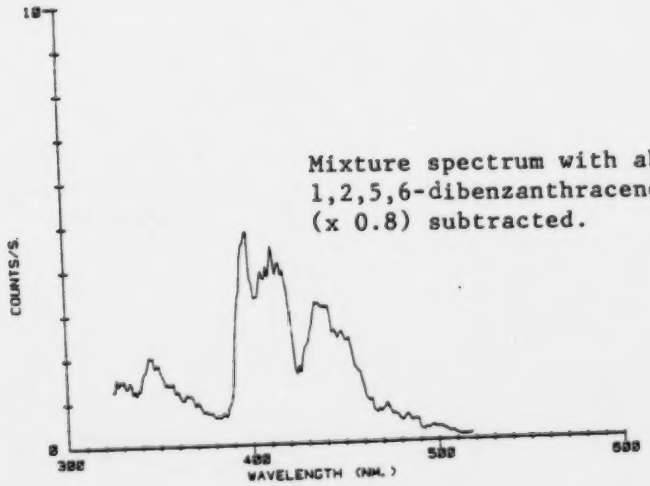
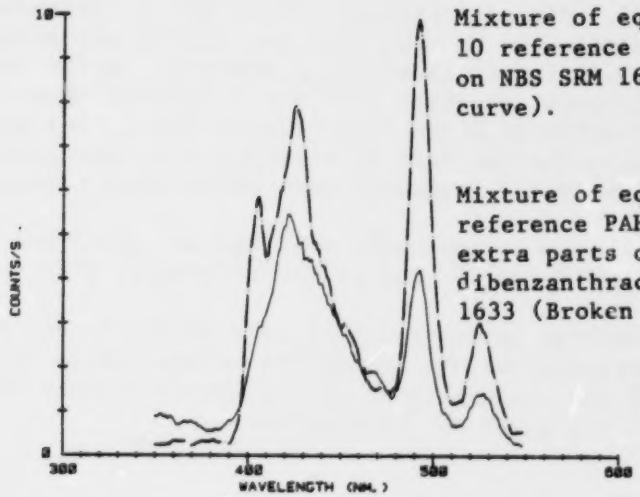
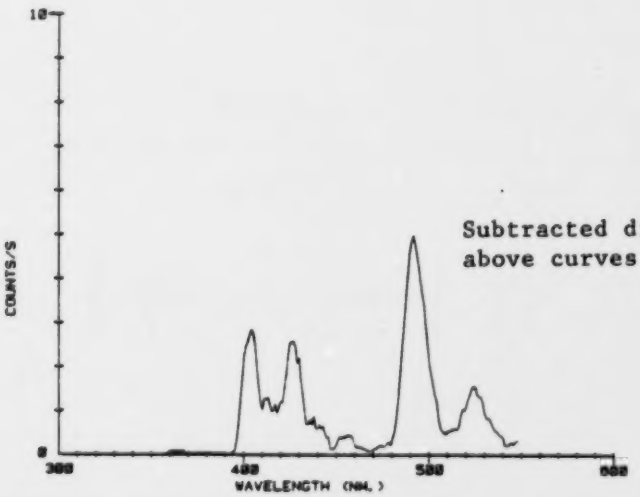


Figure 39. Weighted subtraction of fluorescence components excited at 292 nm of equal parts benzo(k)fluoranthene and 1,2,5,6-dibenzanthracene on NBS SRM 1633.



Mixture of equal parts of 10 reference PAH compounds on NBS SRM 1633 (Solid curve).

Mixture of equal parts of 10 reference PAH compounds plus 5 extra parts of 1,2,5,6-dibenzanthracene on NBS SRM 1633 (Broken curve).



Subtracted difference of above curves.

Figure 40. Subtraction of mixtures of 10 PAH reference compounds showing the presence of 1,2,5,6-dibenzanthracene.

spectrum retains the same peaks as the pure 1,2,5,6-dibenzanthracene on fly ash in Figure 25, but the peak intensities vary, indicating possible interactions between the two compounds. In Figure 39, the 1,2,5,6-dibenzanthracene is subtracted from the mixture to give a spectrum for benzo(k)fluoranthene which corresponds favorably with that in Figure 18 for the pure compound on NBS SRM 1633. The fluorescence spectrum for equal parts of all 10 reference PAHs is presented in Figure 40 along with the spectrum of all 10 compounds with 5 additional parts of 1,2,5,6-dibenzanthracene. The additional 1,2,5,6-dibenzanthracene also produces increased fluorescence from benzo(a)anthracene. The spectrum for the mixture minus the spectrum with the additional 1,2,5,6-dibenzanthracene is presented in the bottom frame of Figure 40. This spectrum shows both the 1,2,5,6-dibenzanthracene and the enhanced contribution from the benzo(a)anthracene. Any multicomponent analysis technique for the PAHs in mixtures must take into account the interactions between the compounds that affect peak intensities.

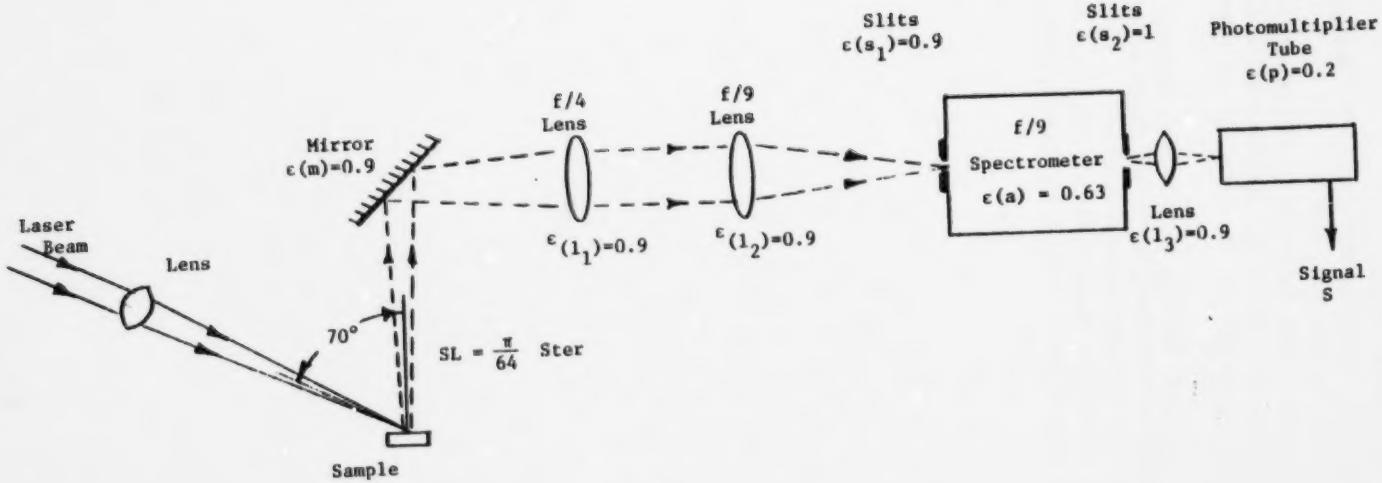
Techniques for multicomponent analysis are described by Stadalius and Gold[5] and Ho and Warner[6] and in the references with these articles.

The instrumental parameters that control the sensitivity of the fluorescence measurements are summarized schematically in Figure 41. The total number of photons generated by the sample between times t_1 and t_2 after the laser pulse are given by the equation:

$$P = \left[\frac{N_1^o \sigma_{12} E_p A_{21} \lambda w x 10^{-7}}{hct_p(A_{21}+q)}\right] x \left\{1-\exp\left[-\left(\frac{\sigma_{12} E_p \lambda x 10^{-7}}{hcA_b t_p} + \frac{\sigma_{21} E_p \lambda x 10^{-7}}{hcA_b t_p} + A_{21} + q\right) t_p\right]\right\} x \exp\left[-\left(A_{21}+q\right) t_2\right] - \exp\left[-\left(A_{21}+q\right) t_1\right] \quad \text{Photons/laser pulse}$$

where

N_1^o = concentration of luminescing species, molecules/cm^3
σ_{12} = absorption cross section, cm^2/molecules
E_p = energy of laser pulse, joule/pulse
A_{21} = Einstein emission coefficient
λ = wavelength of exciting radiation (nm)
w = thickness of luminescing film, cm
h = Planck's constant (6.62×10^{-34} joule-s)



$$S = \frac{\Omega}{4\pi}\ \varepsilon(m)\ e(1_1)\ \varepsilon(1_2)\varepsilon(S_1)\varepsilon(a)\varepsilon(S_2)\varepsilon(1_3)\varepsilon(p)P$$

$$= 2 \times 10^{-4}P \quad \text{photoelectrons/laser pulse}$$

P = total photons/laser pulse

Figure 41. Schematic of detection elements and signal output equation.

c = speed of light (3.00×10^{10} cm/s)
t_p = time duration of laser pulse, s
q = energy transfer coefficient for loss of luminescence
A_b = area of laser beam on sample, cm^2
σ_{21} = stimulated emission cross section, cm^2/molecules
t_1 = time from end of laser pulse to opening of detection window, s
t_2 = time from end of laser pulse to closing of detection window, s

In general, improvements in sensitivity by several orders of magnitude can be achieved over the measurements reported here by increasing laser intensity and the efficiency of the collection within currently achievable limits. For instance, using a smaller f/number spectrometer for collection of fluorescence can increase the signal levels by two orders of magnitude.

SECTION 4

HEAVY METAL ACTIVATED ROOM TEMPERATURE PHOSPHORESCENCE (RTP)

The objective of this part of the program was to evaluate the utility of heavy-metal activated room temperature phosphorescence (RTP) for direct measurements of PAHs on particulate material and to compare this technique with the direct fluorescence approach. The use of heavy-metal activated RTP for the analysis of PAHs deposited on filter paper is well established[8]; however, there is no information on the use of this technique for the direct analysis of PAHs on particulate materials.

EXPERIMENTAL PROCEDURES

The same laser system used for the direct fluorescence measurements was also used for the heavy-metal activated RTP studies. This system had dual channel photon-counting capabilities. Each channel was equipped with gated electronics so that the times of opening and the duration of the times the counting windows were open in each channel could be controlled independently. One window was normally set to measure short-time fluorescence (<100 ns) while the other window was set to measure longer-lived phosphorescence. Pure PAHs and cadmium sulfide, which exhibits long-lived phosphorescence, were used to check the time settings for the gated windows. When the time windows were set so that they were not overlapping, the phosphorescence could be separated from the short-time fluorescence.

A few fluorescence/heavy-metal activated RTP spectra were also recorded with a Perkin-Elmer MPF-44B spectrofluorimeter to provide data comparable to that reported in the literature. Most RTP literature data were obtained with commercial instrumentation and not lasers. The RTP Measurements with the Perkin-Elmer device were not time resolved; so the spectra contained both fluorescence and phosphorescence components.

In preparing heavy-metal activated samples, a number of different procedures were tried. Techniques used for measuring RTP are described by several different investigators[8-22]. It was found that not all the procedures used resulted in samples that produced phosphorescence. The completeness of the drying of a sample was found to be crucial. Also the type of surface was important. In the case where 50μL of 0.5M aqueous lead acetate was mixed with 20 μL of 100 ppm fluoranthene in acetone and deposited on a quartz slide, it required 40 min of drying under an infrared heat lamp for the sample to emit maximum phosphorescence as observed using the Perkin-Elmer fluorimeter. Reduced phosphorescence was observed when drying was incomplete, indicating that phosphorescence intensities may be interpreted incorrectly if the sample is not completely dried.

Sample preparation procedures were also developed for the fly-ash particulate material using fluoranthene and lead acetate. It was also found that drying times of 40 min were required to produce maximum phosphorescence, with both the laser system and the Perkin-Elmer instrument.

RESULTS

Cadmium sulfide and 2-napthalene sulfonate were measured as standards to evaluate the day-to-day performance of the instrumentation. Spectra for these two compounds are shown in Figures 42, 43, and 44.

Heavy-metal activated RTP spectra for fluoranthene on quartz, fly ash, and filter paper are shown in Figures 45, 46, and 47. As has been shown in other RTP studies[23], RTP spectra are sensitive to the type of substrate used. These spectra, all of which involved equal amounts of fluoranthene and lead acetate, show the sensitivity of the spectra to the type of substrate. The lowest detection limit for fluoranthene on fly ash was found to be about 160 ng or 53 µg per g of particles.

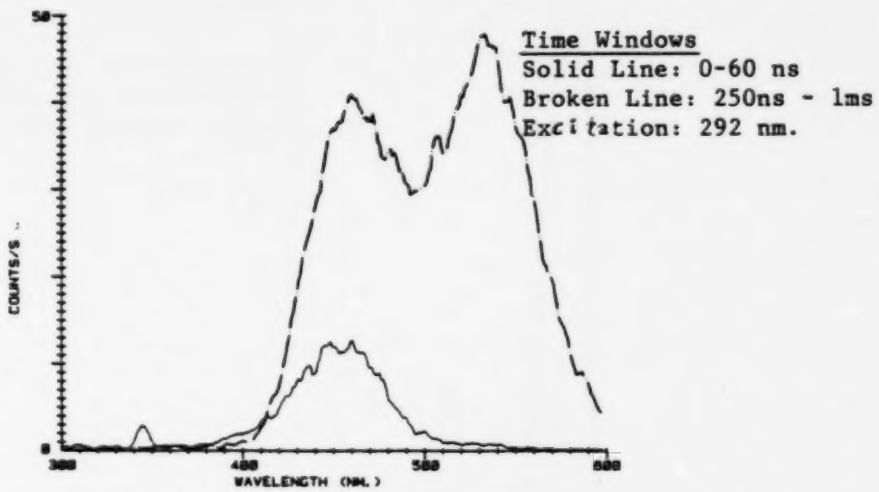


Figure 42. Short-time and long-time components of the luminescence from cadmium sulfide on quartz. (This compound was used to check the separation of time components).

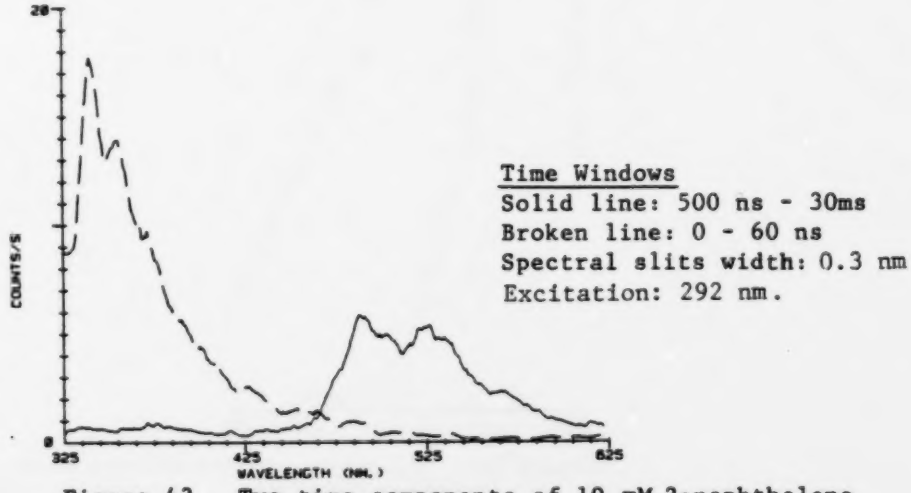


Figure 43. Two time components of 10 mM 2-naphthalene sulfonate on filter paper with 1 M sodium iodide added and dried.

Figure 44. Fluorescence/phosphorescence spectra obtained with Perkin-Elmer MPF-44B spectrofluorimeter for 2-naphthalene sulfonate on quartz filter paper with and without sodium iodide.

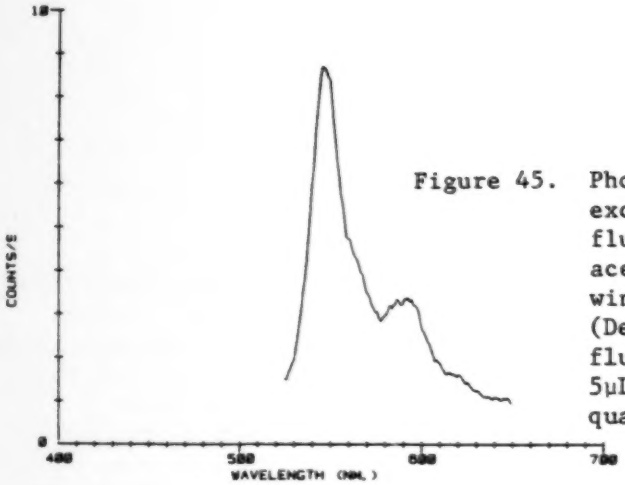


Figure 45. Phosphorescence spectrum excited at 292 nm for fluoranthene and lead acetate on quartz. Time window is 1 μs to 4 ms. (Deposited 5μL of 100 ppm fluoranthene in acetone and 5μL 0.5 M lead acetate on quartz.)

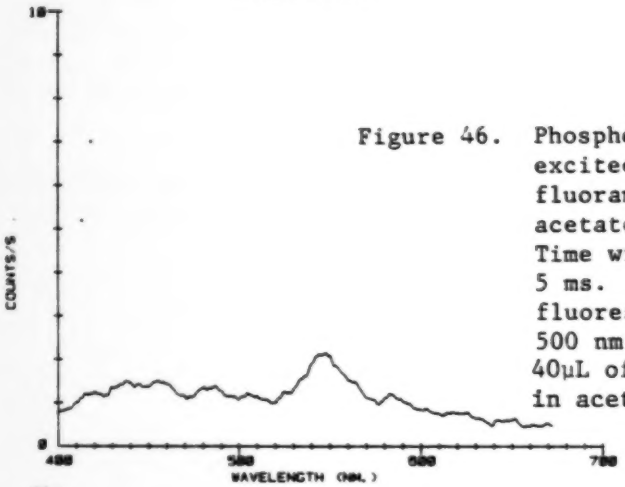


Figure 46. Phosphorescence spectrum excited at 292 nm for fluoranthene and lead acetate on NBS SRM 1633. Time window is 5 μs to 5 ms. (Note the delayed fluorescence in the 400-500 nm region). (Deposited 40μL of 100 ppm fluoranthene in acetone and 40μL 0.5 M lead acetate on 3 mg NBS SRM 1633.)

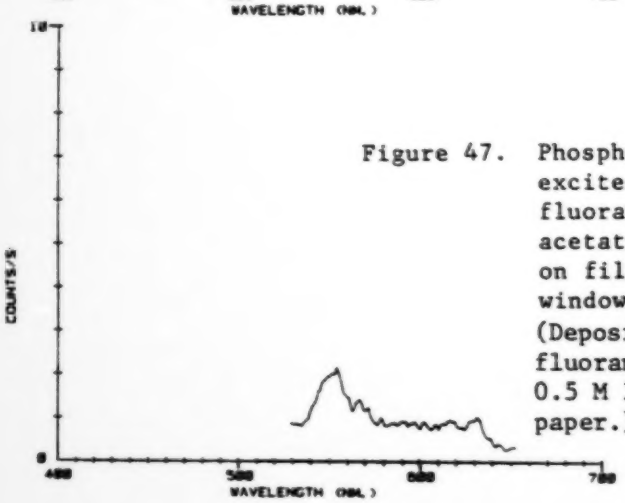


Figure 47. Phosphorescence spectrum excited at 292 nm for fluoranthene and lead acetate mixture deposited on filter paper. Time window is 1 μs to 15 ms. (Deposited 5μL of 100 ppm fluoranthene in acetone and 0.5 M lead acetate on filter paper.)

SECTION 5

OZONE STUDIES

Benzo(a)pyrene was deposited on quartz and exposed to ozone for various periods of time after which fluorescence measurements were made. These results are summarized in Figure 48. The ozone exposure was conducted in the outlet tube of a MEC®-1000 ozonizer where the ozone concentration was about 1 ppmv. A control sample was located near the ozonizer in a hood under conditions equivalent to those for the sample in the ozonizer except that no ozone exposure occurred. The variation in the fluorescence from the control sample is attributed to variations in the deposit distribution and alignment of the sample. Changes in the benzo(a)pyrene spectrum were produced by the ozone exposure. The ratio of the fluorescence intensities at 455 to 425 nm decreased markedly with exposure. Similar changes were also reported by Pitts et al.[7] for benzo(a)pyrene exposed to ozone.

The implications of the decrease in overall fluorescence intensity with exposure to ozone is that some of the benzo(a)pyrene in particulate matter may be converted by ozone into less toxic products.

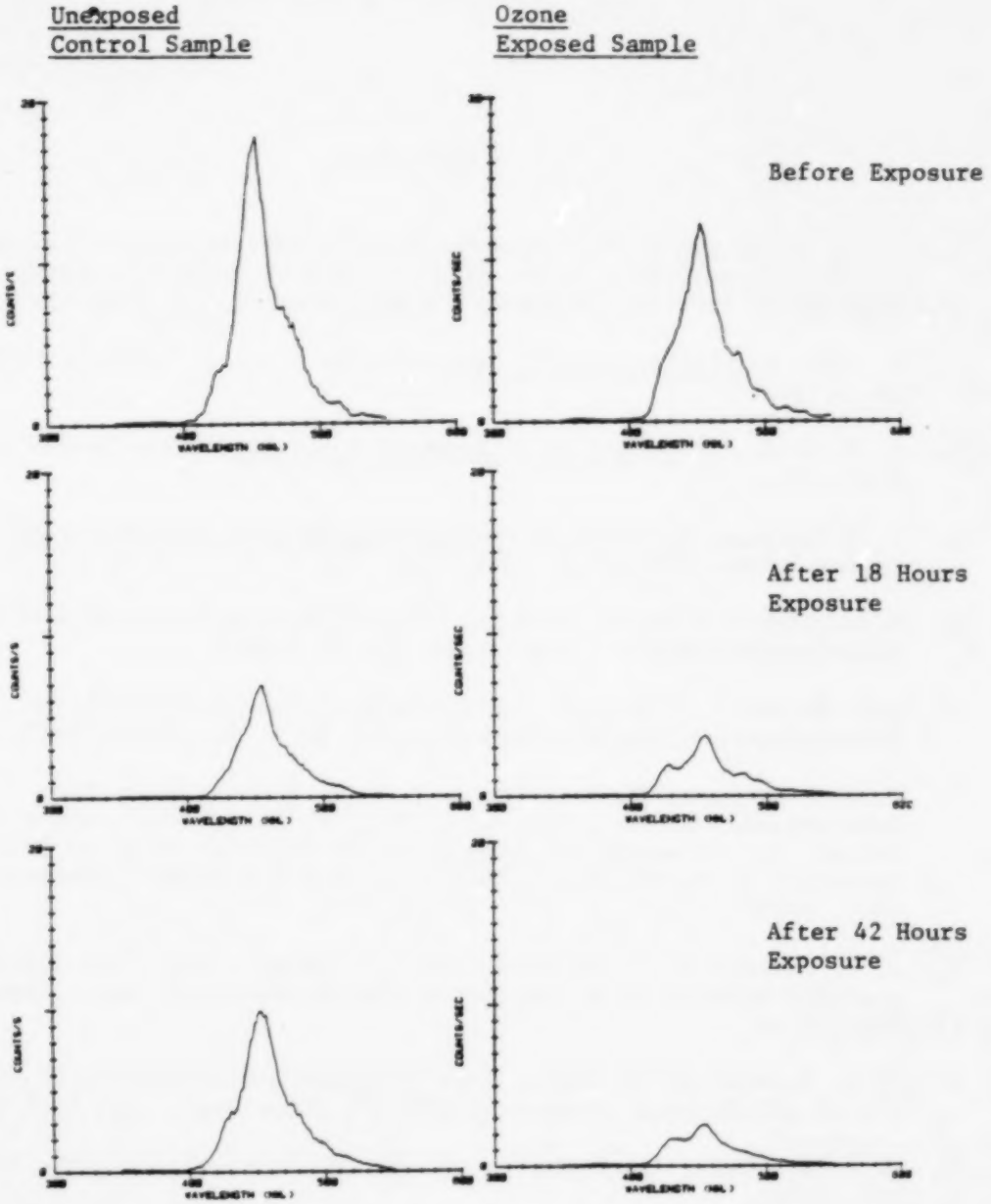


Figure 48. Fluorescence spectra for benzo(a)pyrene deposited on quartz slides with and without exposure to ozone at 1 ppm. These spectra were normalized to 0.3 nm spectral slit width.

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